Optical absorption properties of doped lithium niobate crystals

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Abstract. The optical transmittance of pure lithium niobate ($LiNbO_3$) single crystals and of $LiNbO_3$ single crystals heavily doped with MgO, and double doped with MgO and TiO_2 were measured from the ultraviolet to the visible range with the incident light being perpendicular and parallel, respectively, to the Z axis of the crystals. The wavelength dependence of the absorption coefficient α and its root $\alpha^{1/2}$ (α versus $h\nu$ and $\alpha^{1/2}$ versus $h\nu$, respectively) were calculated and the characteristics of the absorption edges were discussed. The absorption edges below 3.8 eV of all samples are attributable to indirect transition. The energy gaps E_g and E_g' of the crystals, which correspond to the direct transition and the indirect transition, respectively, and the energy of phonons taking part in the indirect transition were calculated. It was found that E_g and E_g' are related to the type and amount of doped ions, and doping with MgO and with TiO_2 will make the energy gap E_g' increase and decrease, respectively, causing the indirect transition absorption edges to move towards the ultraviolet and infrared, respectively.

1. Introduction

Lithium niobate ($LiNbO_3$) crystals doped with some metal oxides have excellent ferroelectric, piezoelectric, electro-optic and non-linear optic properties. They are widely used for making surface acoustic wave (SAW) and optoelectronic devices. Doped $LiNbO_3$ crystals are also ideal objects with which the photoelectronic characteristics and various non-linear cross-coupling effects of crystals can be studied in detail. In the past, some reports on the optical absorption properties of $LiNbO_3$ crystals were published [1, 2]. In this paper, we report the optical absorption—from the ultraviolet to the visible range—properties of pure $LiNbO_3$ crystals and NbO_3 crystals heavily doped with MgO and double doped with MgO and TiO_2 crystals which were newly grown. Because there are three definite straight-line parts in the $\alpha^{1/2}$ versus $h\nu$ curve, we concluded that pure and doped $LiNbO_3$ crystals possess indirect transition properties below 3.80 eV and calculated the energy gaps E_g and E_g' which correspond to the direct transition and the indirect transition, respectively, for all the crystals investigated. It was found that E_g and E_g' are related to the type and amount of doped ions, and doping with MgO and with TiO_2 make the energy gap E_g' increase and decrease, respectively, causing the
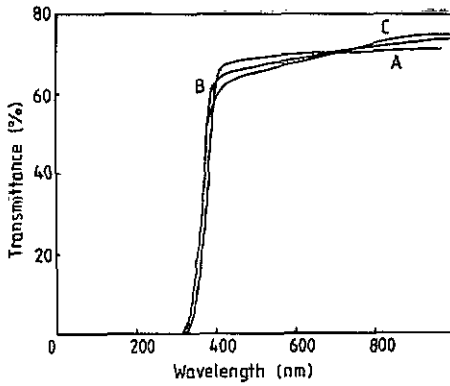
Figure 1. The transmittance curves of LN (curve A), LN:Mg (curve B) and LN:Mg + Ti (curve C) crystals in the ultraviolet and visible ranges (the incident light is perpendicular to the polar axis).

indirect transition absorption edges to move towards ultraviolet and infrared, respectively. The physical interpretation of the three straight-line parts below 3.80 eV in the $\alpha^{1/2}$ versus $h\nu$ curve and the nature of the movement of E'_g and the indirect transition absorption edge of doped LiNbO$_3$ crystals are also given in this paper.

2. Experimental results and data handling

The crystals used in the present work were pure LiNbO$_3$ (LN), LiNbO$_3$ heavily doped with 5–7 mol% MgO (LN:Mg) and LiNbO$_3$ double doped with 5–7 mol% MgO and 0.01–2 mol% TiO$_2$ (LN:Mg + Ti). The crystals with excellent optical homogeneity were newly grown by the modified Czochralski method. The samples were cut perpendicular to the Z axis of the crystals with dimensions of 10 mm × 10 mm × 5 mm (XYZ) for LN, 10 mm × 10 mm × 8 mm for LN:Mg and 10 mm × 10 mm × 5 mm for LN:Mg + Ti, respectively, where the Z axis is the direction of spontaneous polarization.

After mechanical polishing, the optical transmittances of various LiNbO$_3$ samples were measured using a Hitachi 365 recording spectrometer. The results for pure LN, LN:Mg and LN:Mg + Ti are shown in figure 1.

The optical absorption coefficient α of the samples was calculated from the transmittance when the photon energy is below direct energy gap E_g. According to Mclean's formula and the method used in [2], we obtain

$$T = (1 - R)^2 \exp(-\alpha d)/[1 - R^2 \exp(-2\alpha d)] \tag{1}$$

where T is the transmittance, α the absorption coefficient, d the thickness and R the reflectance of the samples.

Equation (1) can be written as

$$\alpha = (1/d)\{2 \ln(1 - R) - \ln T - \ln[1 - R^2 \exp(-2\alpha d)]\}. \tag{2}$$

It follows that, if the dispersion of reflectance R is known, one can calculate from equation (2) the wavelength dependence of absorption coefficient α. Newton's iteration method was employed to obtain the self-consistent solution of equations (1) and (2) by using an IBM-PC computer. This method is slightly different from the method used in [3], and the error resulting from iteration calculation is less than that from approximate calculation used in [2].

According to Fresnel's formula, when incident light is perpendicular to the main surface of the sample, one obtains

$$R_F = [(n-1)^2 + k^2]/[(n+1)^2 + k^2] \tag{3}$$

where R_F is the theoretical reflectance, n the refractive index and k the extinction coefficient. $\alpha = 4\pi k/\lambda$.

In our experiments, λ is in the range 200–800 nm and, when $h\nu > E_g$, α is less than $10^3 \, \text{cm}^{-1}$; therefore $k = \lambda\alpha/4\pi$ is about the order of 10^{-2}. In other words, $n^2 \gg k^2$. So, for simplicity, equation (3) can be rewritten as

$$R = (n-1)^2/(n+1)^2. \tag{3'}$$

Using the Sellmeier's dispersion relation [3] for n, i.e.

$$n^2 = 1 + S\lambda^2/(\lambda^2 - \lambda_S^2) = 1 + S/[1 - (\lambda_S/\lambda)^2] \tag{4}$$

(where S and λ_S are the Sellmeier constants), and the data for the refractive index n of LiNbO₃ crystals given by Nelson and Mikulysk [4], we calculated the theoretical values of the reflectance R_F at individual frequencies.

The real reflectance R' of the samples is often affected by other conditions, such as surface state of the samples and measuring conditions. In a manner similar to that used in [2] and [5], we suggested that, when the transmittance T becomes asymptotically constant, the optical absorption coefficient α is regarded as zero, corresponding to a λ value of near 800 nm (see figure 1). Then, from equation (1), one can get

$$R_0 = (1 - T_0)/(1 + T_0). \tag{5}$$

From equations (1) and (5), we obtained $T_0 = 0.749$ and $R_0 = 0.1435$ for LiNbO₃ samples with incident light perpendicular to the polar axis. On the other hand, when $\lambda = 800$ nm, from equation (3) and the refractive indices given in [4], we obtained $R_F = 0.1369$. The reflectance difference $\Delta R = R_0 - R_F = 0.0066$. We considered that ΔR, which is very small in our experimental conditions, was the same at each wavelength in the visible range. Therefore, the real value $R'(\lambda)$ of the samples was the sum of R_F calculated from equation (3) and ΔR.

By using the experimental curves shown in figure 1 and the method described above, we calculated the frequency dependence of the absorption coefficient α for LN, LN:Mg and LN:Mg + Ti samples with incident light being perpendicular to the polar axis of the samples. The α versus $h\nu$ and $\alpha^{1/2}$ versus $h\nu$ curves are shown in figures 2 and 3, respectively.

3. Discussion

3.1. Forbidden energy gap E_g

It is well known that the fundamental optical transitions include both the direct transition and the indirect transition. The former means that the electrons in the valence band transit vertically to the conduction band under the action of photons. The optical absorption coefficient of the transition is of the order of greater than $10^3 \, \text{cm}^{-3}$. This corresponds to when the transmittance in figure 1 is nearly equal to zero. From the high-energy end of T approaching zero in figure 1, we can obtain that the forbidden energy gaps E_g of LN, LN:Mg and LN:Mg + Ti crystals are 3.80 eV, 3.92 eV and 3.91 eV, respectively.
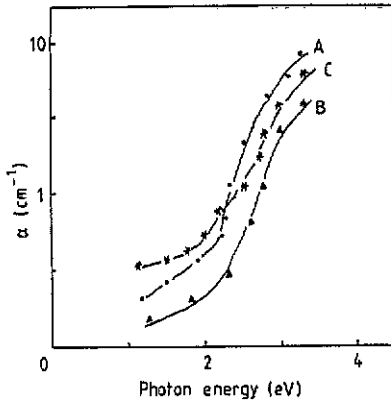
Figure 2. The dependence of absorption coefficient α on the photon energy $h\nu$ for LN (curve A), LN:Mg (curve B) and LN:Mg + Ti (curve C) crystals (the incident light is perpendicular to the polar axis: *, ●, ▲, experimental values; ——, calculated values.
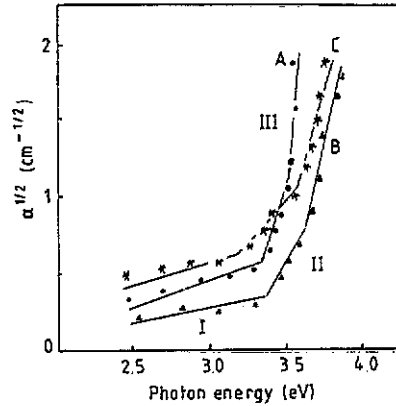
Figure 3. The dependence of the root of absorption coefficient α on photon energy $h\nu$ for LN (curve A), LN:Mg (curve B) and LN:Mg + Ti (curve C) crystals (the incident light is perpendicular to the polar axis: *, ●, ▲, experimental values; ——, calculated values.

3.2. Indirect transition behaviour of the absorption edge below 3.80 eV

As is well known, an indirect transition is a transition with the aid of phonons. If the bottom of the conduction band and the top of the valence band are not at the same wavevector K for a material, an indirect transition may occur with suitable phonons participating. In this transition, the absorption coefficient α is proportional to $(h\nu - E'_g + E_p)^2$ when $h\nu > E'_g - E_p$; corresponding to the absorption of phonons (where $h\nu$, E'_g and E_p are the photon energy, the indirect transition energy gap and the phonon energy, respectively), and α is proportional to $(h\nu - E'_g - E_p)^2$ when $h\nu > E'_g + E_p$, corresponding to the emission of phonons. In both cases, α is less than the order of $10^3 \, \text{cm}^{-1}$.

The electronic energy band structure for LiNbO$_3$ had been given by Kam-Shing Kam *et al* [6]. The top of the valence band and the bottom of the conduction band are at the Γ and X points, respectively, in the Brillouin zone. The smallest and largest valence–conduction band gaps are 3.47 eV and 8.2 eV, respectively. These calculated values are in reasonable good agreement with the existing experimental results [7–9].

Because the bottom of the conduction band and the top of the valence band are not at the same wavevector K for LiNbO$_3$ crystals, an indirect transition may occur with suitable phonons participating. The absorption coefficients which we calculated below 3.80 eV are all less than $10^3 \, \text{cm}^{-1}$. From figure 3 one can find that the $\alpha^{1/2}$ versus $h\nu$ curves have good linear relations below 3.80 eV. All these facts indicate that the absorption edge below 3.80 eV of doped LiNbO$_3$ crystals is an indirect transition in nature.

3.3. Interpretation of three straight-line parts in the $\alpha^{1/2}$ versus $h\nu$ curves

There are three straight-line parts below 3.80 eV in the $\alpha^{1/2}$ versus $h\nu$ curves for LN, LN:Mg and LN:Mg + Ti crystals. The three parts correspond to the slow-drop (weak-absorption), the shoulder and the sharp-drop (strong-absorption) regions, respectively.

These are in agreement with the characteristics of the absorption edges of $SrTiO_3$ [10] and KIO_3 [5] crystals.

From solid state physics one knows that, when the concentration of impurities or defects increases to a certain level in ionic crystals or semiconductors, the energy level of impurities or defects may become wider. This thus forms the band tail which connects to the bottom of the conduction band or the top of the valence band. The greater the concentration of impurities or defects, the wider is the band tail range, resulting in a narrower effective band width. Therefore the transition from certain band-to-band tail states may occur prior to an indirect transition with phonon absorption and be present at the lower-energy end in the absorption spectrum of the indirect transition. From this fact, region I in figure 3 can be regarded as the optical absorption of transitions related to impurities or defects.

For higher-purity crystals, the $\alpha^{1/2}$ versus $h\nu$ curve contains two straight-line parts in the case of indirect transitions, with only a phonon participating. The two parts correspond to photon energy $h\nu > E_g' - E_p$ and $E_g' + E_p$, respectively. Therefore, the difference between the initial energies of the two parts is twice the energy E_p of the phonons which take part in the indirect optical absorption, and their average is the bandwidth E_g' of the indirect transition. From this point of view, regions II and III in figure 3 are attributable to the indirect transition. We calculated E_g' and E_p for LN, LN:Mg and LN:Mg + Ti crystals as follows.

For LN,

$$E_g' = (3.381 + 3.170)/2 = 3.28 \, \text{eV}$$
$$E_p = (3.381 - 3.170)/2 = 0.1055 \, \text{eV} \, (\text{or } 850 \, \text{cm}^{-1}).$$

For LN:Mg,

$$E_g' = (3.528 + 3.321)/2 = 3.42 \, \text{eV}$$
$$E_p = (3.528 - 3.321)/2 = 0.1035 \, \text{eV} \, (\text{or } 835 \, \text{cm}^{-1}).$$

For LN:Mg + Ti,

$$E_g' = (3.351 + 3.140)/2 = 3.25 \, \text{eV}$$
$$E_p = (3.351 - 3.140)/2 = 0.1055 \, \text{eV} \, (\text{or } 850 \, \text{cm}^{-1}).$$

The Raman spectrum of these samples shows that the intensity of phonons at 883 and $632 \, \text{cm}^{-1}$ are very strong and their frequencies are the highest of all phonons recorded. Thus, it is reasonable to conclude that the indirect transition of doped $LiNbO_3$ crystals is due to the common contribution of 883 and $632 \, \text{cm}^{-1}$ phonons.

3.4. The movement of the indirect transition energy gap E_g' and the indirect transition absorption edge of doped LiNbO₃ crystals

From figure 3 and the discussion above, we can see that the indirect transition energy gap E_g' of LN:Mg is the highest and that of LN:Mg + Ti the lowest of the three crystals discussed. In other words, it is a rational conclusion that doping with MgO will make the indirect transition energy gap E_g' of $LiNbO_3$ crystals increase, causing the indirect transition absorption edge of LN:Mg to move towards the ultraviolet. This is in agreement with the results of Polgar *et al* [11]. It is also reasonable to conclude that doping

with TiO_2 will make the indirect transition energy gap E'_g of $LiNbO_3$ crystals decrease, causing the indirect transition absorption edge of LN:Ti crystals to move towards the infrared. In order to verify this conclusion further, we measured the optical transmissivity for a series of $LiNbO_3$ crystals doped with different amounts of MgO and TiO_2, with incident light both perpendicular and parallel to their Z axes, and calculated E_g, E'_g and E_p for each sample using the same method. It is certain from these results that doping with MgO and with TiO_2 will make the indirect transition energy gap E'_g of $LiNbO_3$ crystals move towards the ultraviolet and infrared, respectively.

According to the theory of Didomenico and Wemple [12], the intensity of the Nb–O band will affect the forbidden band width directly. Being doped with different metal oxides, the distortion of oxygen octahedron of $LiNbO_3$ crystals will change in varying degrees. It is evident that the extent of the distortion of oxygen octahedron will affect the intensity of the Nb–O bond, resulting in a change in the energy band structure of the crystals. The change in band structure may be different at different symmetric points in the Brillouin zone. We suggest that, compared with pure $LiNbO_3$ crystals, doping with MgO will make the bottoms of the conduction band at the X and Γ points move upwards and downwards, respectively (on the assumption that the top of the valence band at the Γ point remains unchanged) causing the indirect transition energy gap E'_g of LN:Mg crystals to increase and the indirect transition absorption edge of LN:Mg crystals to move towards the ultraviolet. For the same reason, we suggest that doping with TiO_2 will make the bottoms of the conduction band at the X and Γ points move downwards and upwards, respectively (also on the assumption that the top of the valence band at the Γ point remains unchanged), causing the E'_g for LN:Mg + Ti crystals to decrease and the indirect transition absorption edge of LN:Mg + Ti crystals to move towards the infrared.

4. Conclusions

With incident light perpendicular and parallel to their polar axes, respectively, the transmittances of LN, LN:Mg and LN:Mg + Ti were recorded from the ultraviolet to vissible range. From transmittance curves and the $\alpha^{1/2}$ versus $h\nu$ curves we calculated the direct transition energy gap E_g, the indirect transition energy gap E'_g and the energy E_p of phonons taking part in the indirect transitions of all the samples. It was found that doping with MgO or with TiO_2 makes the indirect transition energy gap E'_g of $LiNbO_3$ crystals increase or decrease causing the indirect transition absorption edges to move towards the ultraviolet or infrared, respectively. The movement of the E'_g of doped $LiNbO_3$ crystals may be attributable to the distortion of electronic energy band structures resulting from the introduction of doped ions.

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